

## **CHAPTER 3**

### **EPA/NSF ETV EQUIPMENT VERIFICATION TESTING PLAN COAGULATION AND/OR CO-PRECIIPITATION AND FILTRATION FOR REMOVAL OF ARSENIC**

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## APPENDICES

Appendix A Arsenic Speciation Method Developed by Battelle for EPA

## 1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN

This document is the Environmental Technology Verification (ETV) Technology Specific Test Plan (TSTP) for evaluation of water treatment equipment for arsenic removal utilizing chemical coagulation and filtration processes. This TSTP is to be used as a guide in the development of Product Specific Test Plan (PSTP) procedures for testing coagulation and filtration equipment, within the structure provided by the “EPA/NSF ETV Protocol for Equipment Verification Testing For Arsenic Removal: Chapter 1, Requirements for All Studies.” This TSTP was originally developed for use with granular media filtration processes that rely upon chemical coagulation to effectively condition the feed water for effective filtration. Other approaches to arsenic removal by coagulation and filtration may be utilized, including oxidation and co-precipitation of naturally occurring iron and arsenic in water, to facilitate removal by coagulation and filtration. Furthermore, filtration processes other than granular media might be utilized. For these reasons the original TSTP for removal of arsenic by coagulation and filtration has been modified to reflect the numerous options for treatment that exist. Where appropriate, other TSTPs are referenced.

To participate in the equipment verification process for coagulation and filtration, the equipment manufacturer shall employ the procedures and methods described in this TSTP and in the referenced ETV protocol document as guidelines for the development of the PSTP. The procedures shall generally follow those tasks related to verification testing that are outlined herein, with changes and modification made for adaptations to specific equipment. At a minimum, the format of the procedures written for each task should consist of the following sections:

- Introduction;
- Objectives;
- Work Plan;
- Analytical Schedule; and
- Evaluation Criteria.

Each PSTP shall include Tasks 1 through 6.

## 2.0 INTRODUCTION

Various types of water treatment equipment employing processes of coagulation and filtration are used for a wide number of applications, including removal of turbidity from surface waters; removal of pathogens such as bacteria, viruses, *Giardia* and *Cryptosporidium*; removal of algae, color, and other natural organic matter from surface waters; and removal of inorganic constituents such as arsenic. Some equipment process trains use only chemical coagulation, mixing, and granular media filtration while others employ a solids separation or clarification step between coagulation and filtration. Clarification processes may include one of the following:

- Sedimentation;
- Sedimentation aided by tubes or plates;

- Downflow contact clarification;
- Upflow contact clarification; and
- Dissolved air flotation (DAF).

Filtration processes that could be tested include the following:

- Granular media filters;
- Membrane filters;
- Precoat filters;
- Bag filters;
- Cartridge filters; and
- Backwashable depth filters.

This TSTP is applicable to the testing of water treatment equipment utilizing a coagulation and filtration process train, which may include a clarification step before filtration. Two phases of testing are discussed. The first phase is initial operations, which consists of a series of tests that will be used to determine the optimum chemical pretreatment scheme at a specific geographic location. The second phase is verification testing, which will evaluate performance of the equipment under different raw water quality conditions. Verification tests will be performed for relatively short time intervals during one or more periods when the source water or feed water quality is appropriate for testing the range of water quality conditions that need to be evaluated.

Several of the arsenic studies referenced in this TSTP have shown that As (V) removal by coagulation and filtration is much more effective than As (III) removal. Thus, a preferred approach to arsenic treatment may involve pre-oxidation to convert all arsenic to As (V) so the most effective results will be attained. This optional additional treatment procedure is discussed where appropriate.

### **3.0 GENERAL APPROACH**

Testing of equipment covered by this TSTP will be conducted by a Field Testing Organization (FTO) that is qualified by NSF International (NSF) and is selected by the manufacturer. Water quality analytical work to be carried out as a part of this TSTP shall be contracted with a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA.

### **4.0 OVERVIEW OF TASKS**

The following section provides a brief overview of the recommended tasks that may be included in initial operations and of the tasks required to be included in the coagulation and filtration verification testing program.

#### **4.1 Task A: Characterization of Feed Water**

The objective of this recommended initial operations task is to obtain a chemical and physical characterization of the feed water. A brief description of the watershed that provides the feedwater shall be provided to aid in interpretation of feedwater characterization.

#### **4.2 Task B: Initial Tests Runs**

During initial operations, a manufacturer may want to evaluate equipment operation and determine the chemical dosages and other pretreatment conditions that result in effective treatment of the feed water. This is a recommended initial operations task.

#### **4.3 Task 1: Verification Testing Runs**

Water treatment equipment shall be operated for at least 320 hours during one or more testing periods to collect data on equipment performance and water quality for purposes of performance verification. Length of operation depends on the filtration process used.

#### **4.4 Task 2: Feed Water and Finished Water Quality**

During verification testing, feed water and treated water samples shall be collected, and appropriate sample analysis shall be undertaken. For example, turbidity samples are needed to determine the efficiency of surface water treatment, in addition to arsenic analyses for the evaluation of arsenic removal.

#### **4.5 Task 3: Operating Conditions and Treatment Equipment Performance**

During verification testing, operating conditions and performance of the water treatment equipment shall be documented. Operating conditions include pretreatment chemistry for coagulation, a listing of treatment processes used, and their operating conditions. If pre-oxidation is used, performance of this equipment shall be documented. Equipment performance information includes data such as rate of filter head loss gain, duration of filter runs and volume of water filtered per run, frequency and duration of filter cleaning, filter changing or replacement, and need for cleaning of pretreatment clarifiers. The operating conditions shall include plant flow rates and chemical dosages.

#### **4.6 Task 4: Arsenic Removal**

The objective of this task is to evaluate arsenic removal during verification testing by measuring arsenic in the feed water and in the treated water. If the arsenic concentration naturally present in the feed water is not sufficiently high for testing, arsenic spiking is needed. In addition detailed data on coagulant dosages and pre-oxidants, if used, are to be collected.

## **4.7 Task 5: Data Management**

The objective of this task is to establish an effective field protocol for data management at the field operations site and for data transmission between the FTO and NSF for data obtained during the verification testing, plus the requirement for statistical analysis of the data.

## **4.8 Task 6: Quality Assurance and Quality Control**

An important aspect of verification testing is the protocol developed for quality assurance and quality control (QA/QC). The objective of this task is to assure accurate measurement of operational and water quality parameters during coagulation and filtration equipment verification testing.

## **5.0 TESTING PERIODS**

The required tasks in this TSTP (Tasks 1 through 6) are designed to be carried out over one or more testing periods having a duration of at least 320 hours, not including the time required for mobilization, start-up, and initial operations. Length of operation depends on the filtration process used. A schedule describing the duration of testing periods for various filtration processes is provided in Table 1.

## **6.0 DEFINITIONS**

Definitions that apply for coagulation and filtration processes and that were given in the Surface Water Treatment Rule, as published in the *Federal Register* on June 29, 1989, are:

**6.1 Coagulation:** A process using coagulant chemicals and mixing by which colloidal and suspended materials are destabilized and agglomerated into flocs.

**6.2 Conventional filtration treatment:** A series of processes including coagulation, flocculation, sedimentation, and filtration resulting in substantial particulate removal.

**6.3 Direct filtration:** A series of processes including coagulation and filtration but excluding sedimentation which results in substantial particulate removal.

**6.4 Filtration:** A process for removing particulate matter from water by passage through porous media.

**6.4.1 Granular media filtration:** Filtration through a bed of granular material such as sand, anthracite coal, garnet, ilmenite, granular activated carbon, or other material suitable for use as filter media.

**6.4.2 Membrane filtration:** Filtration using a microfiltration or ultrafiltration membrane.



**6.4.3 Precoat filtration:** A process resulting in substantial particulate removal in which (1) a cake of precoat filter media is deposited on a support membrane (septum), and (2) while the water is filtered by passing through the cake on the septum, additional filter media known as body feed is continuously added to the filter cake to maintain the permeability of the filter cake.

**6.4.4 Bag filtration:** Filtration using a non-rigid, disposable, fabric filter in which flow generally is from the inside of the bag to the outside. One or more filter bags are contained within a pressure vessel designed to facilitate rapid change of the filter bags when the filtration capacity has been used up.

**6.4.5 Cartridge filtration:** Filtration using a rigid or semi-rigid, disposable, self-supporting filter element in which flow generally is from the outside of the cartridge to the inside. One or more filter cartridges are contained within a pressure vessel designed to facilitate rapid change of the cartridges when the filtration capacity has been used up.

**6.5 Flocculation:** A process to enhance agglomeration or collection of smaller floc particles into larger, more easily settleable particles through gentle stirring by hydraulic or mechanical means.

**6.6 Sedimentation:** A process for removal of solids before filtration by gravity or separation.

Other definitions include:

**6.7 Dissolved air flotation:** A process in which coagulated, flocculated water is introduced into the bottom of a chamber, along with recycled water containing microscopic air bubbles. The bubbles attach to the floc and rise to the water surface, carrying the floc up, while the clarified water leaves the chamber near the bottom.

**6.8 Contact clarification:** A process in which coagulated water is applied to a bed of coarse granular media. Flow may be downward from the top of the media bed to the bottom, or upward from the bottom of the media bed to the top. The bed of coarse media acts both as a flocculator by causing the division and recombination of flow streams of coagulated water, and as a clarifier, by trapping and removing some of the floc that forms as water flows through the bed. The coarse granular media may consist of natural mineral material or man-made materials such as plastic.

**6.9 Surface water:** All water which is open to the atmosphere and subject to surface runoff. For purposes of this document, surface water includes water from surface sources such as lakes, reservoirs, canals, rivers, or streams; and it also includes ground water under the direct influence of surface water.

**6.10 Groundwater:** For purposes of this testing program, groundwater is defined by *The Drinking Water Dictionary* as: The water contained in interconnected pores located (1) below the water table in an unconfined aquifer or (2) in a confined aquifer.

## **7.0 TASK A: CHARACTERIZATION OF FEED WATER**

### **7.1 Introduction**

The initial operations task is needed to determine if the chemical, biological and physical characteristics of the feed water are appropriate for the water treatment equipment to be tested.

### **7.2 Objective**

The objective of this task is to obtain a complete chemical, biological, and physical characterization of the source water or the feed water that will be entering the treatment system being tested.

### **7.3 Work Plan**

This task can be accomplished by using analytical measurements obtained from third party sources (i.e. United States Geological Survey (USGS), U.S. EPA, State Laboratories, Municipal Laboratories). The specific parameters needed to characterize the water will depend on the equipment being tested but information on the following characteristics should be compiled:

- Water temperature, pH, turbidity, and arsenic concentration and species;
- Total alkalinity, calcium hardness, iron, manganese, sulfate, silica and fluoride; and
- Algae, color, and total organic carbon (TOC).

Sufficient information should be obtained to illustrate the variations expected to occur in the water source during an annual cycle for the parameters that will be measured during verification testing. . This information will be compiled and shared with NSF so NSF and the FTO can determine the adequacy of the data for use as the basis to make decisions on the testing schedule. Failure to adequately characterize the feed water (source water) could result in testing at a site later deemed inappropriate, so the initial characterization will be important to the success of the testing program. Hering et al. (1997) have shown that under certain conditions, source water composition can influence arsenic removal by coagulation and filtration, so a good understanding of source water composition could be important to the outcome of verification testing. If removal of arsenic by pre-oxidation and co-precipitation with naturally occurring iron is contemplated, careful documentation of the concentrations of arsenic and iron in the feed water prior to verification testing are essential.

A brief description of the watershed that provides the feedwater shall be provided to aid in interpretation of feedwater characterization. The watershed description should include:

- Approximate size;
- Topography (i.e. flat, gently rolling, hilly, mountainous);
- Types of human activities that take place (i.e. mining, manufacturing, cities or towns, farming);
- Potential sources of pollution influencing water quality, especially potential sources for arsenic discharge; and

- Nature of the water source, such as stream, river, lake, wells, or man-made reservoir.

## **7.4 Analytical Schedule**

In many cases, sufficient water quality data may already exist in the determination of the suitability of a source water for use as feedwater in a coagulation and filtration verification testing program.

## **7.5 Evaluation Criteria**

Feed water quality will be evaluated in the context of the manufacturer's statement of performance objectives. The feed water should challenge the capabilities of the equipment but should not be beyond the range of water quality suitable for treatment for the equipment in question. For example, if the manufacturer's equipment is only capable of treating a maximum arsenic influent concentration of 200 µg/L, it would not be appropriate to test a feedwater containing an influent arsenic concentration of 300 µg/L.

# **8.0 TASK B: INITIAL TEST RUNS**

## **8.1 Introduction**

During initial operations, a manufacturer may want to evaluate equipment operation and determine the chemical dosages and other pretreatment conditions that result in effective treatment of the feed water. This is a recommended initial operations task. An NSF field inspection of equipment operations and sampling and field analysis procedures may be carried out during the initial test runs.

## **8.2 Objective**

The objective of the test runs is to determine the proper chemical pretreatment scheme for treatment of the feedwater during verification testing. The chemical pretreatment requirements may be different for feedwaters from different test sites, different sources, or for the feedwater from the same site during testing periods when water quality has changed from the quality encountered during an earlier testing period. Therefore, conducting initial test runs is strongly recommended.

## **8.3 Work Plan**

Before runs are made in which coagulant is used, the equipment shall be operated with uncoagulated feed water (spiked with arsenic if necessary) for one 24-hour run, and samples shall be collected from the feed water, clarifier effluent, and the filter effluent at 6, 12, 18, and 24 hours of operation to determine if arsenic losses occur through the system. Even though this test run is made during the initial operations, the data shall be presented in the verification testing report.

Conducting jar tests is often a cost effective means of developing data on coagulant chemical dosages and pH that give effective coagulation. The use of jar tests is recommended before filtration testing is initiated. The American Water Works Association's (AWWA) Manual M37 (1992) contains a chapter that describes procedures for using jar tests to optimize coagulation. Tests conducted for the effectiveness of both alum and iron as inorganic coagulants may be appropriate. The effect of polymer addition as a coagulant aid, and the effect of pH adjustment (acid or base addition) could also be examined through jar tests. Extensive bench-scale coagulation studies of arsenic removal have been performed previously at different test sites to determine arsenic removal, as demonstrated by various researchers (Sorg and Logsdon, 1978; Cheng, *et al.*, 1994).

After jar tests have identified effective treatment conditions, several test runs may be needed to further refine appropriate chemical pretreatment conditions. At the end of these tests, an effective chemical pretreatment scheme should have been defined. During initial operations, the filters should be operated for a period of 24 hours, or for filter run times as long as those anticipated during verification testing. The use of bench-scale tests followed by pilot-scale coagulation tests, using alum and ferric chloride, is documented in a study performed by Cheng, *et al.* (1994), and may be used as a guide for performing this phase of testing.

For equipment that uses naturally occurring iron in groundwater as the coagulant chemical for attaining arsenic removal, initial test runs should include frequent measurement of iron and arsenic in the source water to indicate the extent of variability of these constituents. Sorg (2002) has described a range of arsenic and iron concentrations in which removal of iron can result in effective arsenic removal by coagulation and filtration. Sorg suggested that for effective removal of arsenic by natural iron, the natural iron concentration should be at least 0.3 mg/L, and the ratio of iron to arsenic (the Fe:As ratio) should be 20:1 or greater.

Filters will be operated until either terminal headloss is reached or effluent turbidity increases above a value recommended by the manufacturer (but not higher than 5 NTU).

#### **8.4 Analytical Schedule**

Because these runs are being conducted to define operating conditions for verification testing, a strictly defined schedule for sampling and analysis may not need to be followed. Adhering to the schedule for sampling and analyses to be followed during verification testing would be wise so that the operator can gain familiarity with the time requirements that will be applicable later on in the test program. Also, during the initial operations phase, NSF may conduct an initial on-site inspection of field operations and sampling activities. The sampling and analysis schedule for verification testing shall be followed during the on-site inspection.

#### **8.5 Evaluation Criteria**

The manufacturer should evaluate the data produced during the initial operations to determine if the water treatment equipment performance met or exceeded expectations based on the statement of performance objectives. If the performance was not as good as the statement of performance

objectives, the manufacturer may wish to conduct more initial operations or to cancel the testing program.

## **9.0 TASK 1: VERIFICATION TESTING RUNS**

### **9.1 Introduction**

Drinking water treatment equipment employing coagulation and filtration shall be operated for verification testing purposes, with the approach to coagulation based on the results of the initial operations testing. If pre-oxidation is included in the equipment being tested and pre-oxidation is necessary for effective equipment performance, that process equipment shall be operated also.

### **9.2 Experimental Objective**

The objective of this task is to operate the treatment equipment provided by the manufacturer and to assess its ability to meet the water quality goals and any other performance characteristics specified by the manufacturer in the statement of performance objectives.

### **9.3 Work Plan**

#### **9.3.1 Verification Testing Runs**

The verification testing runs in this task consist of continued evaluation of the treatment system, using the most successful treatment parameters defined in initial operations. To obtain a perspective on the influence of feed water quality on arsenic removal by coagulation and filtration, and on the overall performance of the equipment, one or more verification testing periods, each lasting for a minimum of 320 hours (the equivalent of 13 full days plus one 8-hour shift), are anticipated for evaluating the performance of a treatment system. During each of these testing periods, Tasks 2 through 5 shall be conducted within the time frame for carrying out Task 1. Table 1 lists filtration processes that might be used, and states requirements for minimum duration of operation for verification testing for different filtration processes.

Operation under a variety of water quality conditions is recommended because of the differences in water quality that occur over time in many source waters. For coagulation and filtration treatment equipment, factors that can influence treatment performance include:

- Cold water, encountered in winter or at high altitudes in mountainous regions;
- High turbidity, often occurring in spring, encountered in rivers carrying a high sediment load or in surface waters during periods of high runoff resulting from heavy rains or snowmelt;
- Algae, which may bloom on a seasonal basis such as in summer or fall;
- Natural organic matter (NOM), which may be higher in some waters in the fall;
- pH, alkalinity, and hardness, which may vary over time; and

- Sulfate can influence arsenic removal (Hering et al. 1997).

It is highly unlikely that all of the above problems would occur in a surface water during a single test period. Although one testing period satisfies the minimum requirement of ETV, manufacturers are encouraged to use additional testing periods to cover a wider range of water quality conditions. Testing a water which has little change in quality over time could result in acceptance of equipment for use only in water having a narrow range of water quality.

For evaluation of arsenic removal by coagulation and filtration using a process other than granular media, information on factors to evaluate in the verification testing runs can be obtained by referring to the “ETV Protocol for Equipment Verification: Testing for Physical Removal of Microbiological and Particulate Contaminants” and a TSTP for one of the following:

- Membrane Filtration for the Removal of Microbiological and Particulate Contaminants;
- Bag Filters and Cartridge Filters for the Removal of Microbiological and Particulate Contaminants;
- Precoat Filtration for the Removal of Microbiological and Particulate Contaminants; or
- Backwashable Depth Filtration for the Removal of Microbiological and Particulate Contaminants.

### **9.3.2 Routine Equipment Operation**

If the water treatment equipment is being used for production of potable water and treats a water that naturally contains concentrations of arsenic appropriate for verification testing, so that arsenic spiking is not needed, routine operation for water production is anticipated in the time intervals between verification runs. The operating and water quality data collected and furnished to the Safe Drinking Water Act (SDWA) primacy agency during these times shall also be supplied to the FTO.

## **9.4 Schedule**

To meet the goals of the verification testing for equipment employing coagulation and granular media filtration, the following conditions shall be met:

- Water treatment equipment shall be operated continuously for a minimum of 320 hours (the equivalent of 13 full days plus one 8-hour work shift);
- During this time, treatment equipment shall be operated continuously from start-up until turbidity breakthrough or terminal head loss is attained;
- Interruptions in filtration shall occur only as needed for backwashing of the filters or contact clarification pretreatment unit;
- Filter runs shall not be stopped before turbidity breakthrough or terminal head loss is achieved, with the exception of equipment failure or power interruption;

- The duration of each filter run and the number of gallons of water produced per square foot of filter area shall be recorded in the operational results; and
- During routine equipment operation, the water treatment equipment should be operated to meet the system demands and water quality requirements.

Schedules for operation of other filtration processes are found in the TSTPs that have been developed for evaluation of those processes.

## **9.5 Evaluation Criteria**

The goal of this task is to operate the coagulation and filtration equipment for the time required in Table 1, including time for filter cleaning and other necessary operating activities, during verification testing. Data shall be provided to substantiate the operation for the required time.

## **10.0 TASK 2: FEED WATER AND FINISHED WATER QUALITY**

### **10.1 Introduction**

Water quality data shall be collected for the feedwater and filtered water as shown in Table 2, during verification testing. At a minimum, the required sampling schedule shown in Table 2 shall be observed by the FTO. Water quality goals and target removal goals for the water treatment equipment shall be recorded in the PSTP in the statement of objectives.

### **10.2 Experimental Objectives**

A list of the minimum number of water quality parameters to be monitored during equipment verification testing is provided in the analytical schedule section below and in Table 3. The actual water quality parameters selected for testing shall be stipulated in the PSTP procedures and shall include all those necessary to permit verification of the statement of performance objectives.

### **10.3 Work Plan**

The FTO will be responsible for establishing the equipment operating parameters on the basis of the initial operations testing. The filter shall be operated continuously until turbidity breakthrough or terminal headloss is attained, at which time it shall be backwashed.

Some of the water quality parameters described in this task will be measured on-site by the FTO (refer to Table 3). Analysis of the remaining water quality parameters will be performed by a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA. The methods to be used for measurement of water quality parameters in the field are described in Table 3. The analytical methods utilized in this study for on-site monitoring of feedwater and filtered water qualities are discussed in Task 6, Quality Assurance/Quality Control. Where appropriate, the *Standard Methods* reference numbers for water quality parameters are provided for both the field and laboratory analytical procedures.

### **10.3.1 Water Quality Sample Collection**

Water quality data shall be collected during each period of filtration testing, as noted in this section. Additional sampling and data collection may be performed at the discretion of the manufacturer. Sample collection frequency and protocol shall be defined in the PSTP.

In the case of water quality samples that will be shipped to the State or EPA-accredited analytical laboratory for analysis, the samples shall be collected in appropriate containers (containing preservatives as applicable) prepared by the state or EPA-accredited analytical laboratory. These samples shall be preserved, stored, shipped and analyzed in accordance with appropriate procedures and holding times, as specified by the analytical laboratory.

## **10.4 Analytical Schedule**

During verification testing for coagulation and filtration treatment equipment, the feed water (raw water) quality, filtered water quality, (and if applicable, the clarified water quality) shall be characterized by measurement of the following water quality parameters. For pH samples, the treated water pH must be the pH of the coagulated water because coagulation pH can have a strong influence on arsenic removal. If any pH adjustment is made after coagulation, this also must be noted. Water quality samples, whether designated for collection at maximum intervals of once per day or once per week shall be obtained during each arsenic challenge test that involves distinct treatment conditions, even if this increases the water quality sample collection frequency to greater than once per week.

- Temperature (daily);
- pH (daily and in conjunction with arsenic sample collection);
- Total alkalinity (daily);
- Hardness (weekly or once during each set of treatment conditions for which arsenic sampling is done);
- TOC (weekly or once during each set of treatment conditions for which arsenic sampling is done);
- UV<sub>254</sub> absorbance (weekly or once during each set of treatment conditions for which arsenic sampling is done);
- Turbidity (daily at bench to check continuous turbidimeters);
- Aluminum (daily if an aluminum salt coagulant is used and each time when arsenic sampling is done and alum is the coagulant chemical; sampled weekly if aluminum coagulant not used.);
- Iron (daily if iron coagulant is used and each time when arsenic sampling is done and iron is the coagulant chemical; sampled weekly if iron is not used to co-precipitate with arsenic.);
- Manganese (weekly or once during each set of treatment conditions for which arsenic sampling is done if above 0.05 mg/L in feed water);
- Algae, number and species (weekly or once during each set of treatment conditions for which arsenic sampling is done);



- True color (weekly or once during each set of treatment conditions for which arsenic sampling is done);
- Sulfate (weekly);
- Dissolved oxygen concentration in feed water (daily);
- Dosage of pre-oxidation chemical and residual concentration after filter (if a preoxidation chemical was used) (only in Task 4, every 6 hours to coincide with arsenic sampling); and
- Arsenic (see Task 4).

The above water quality parameters are listed to provide verification report readers with background data on the quality of the feed water being treated and the quality of the filtered water. These data are to be collected to enhance the usefulness of the verification testing data to a wide range of verification report readers. Data on feed water need to be obtained because of the possibility that feed water composition could influence arsenic removal performance for some operating variables, including coagulation pH, coagulant chemical used, and valence state of the arsenic.

Additionally, at the end the verification test, samples of the sludge generated shall be collected to assess the chemical content for disposal purposes. At least one representative sample of the sludge shall be collected and sent to the laboratory for the Toxicity Characteristic Leaching Procedure (TCLP) and the California Waste Extraction Test (WET). The FTO shall describe the sampling procedures that will be used to ensure that a representative sample of the sludge is collected for these analyses. The sample that is collected for TCLP and California WET shall have the following metals analyzed in the leachate from these procedures: As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Se, Ag, and Zn.

## **10.5 Evaluation Criteria**

Performance shall be evaluated in the context of the manufacturer's statement of performance objectives.

If iron coagulant is used or if natural iron is oxidized so it can act as a coagulant, the filtered water data shall be tabulated and the concentration of iron in filtered water shall be compared to the secondary Maximum Contaminant Level (MCL) of 0.3 mg/L. If aluminum coagulant is used, the residual aluminum concentration in filtered water samples shall be tabulated.

Also, turbidity results for systems treating surface waters or ground water under the influence of surface water shall be analyzed to determine the percentage of turbidity data in the range of 0.10 NTU or lower, the percentage in the range of 0.11 NTU to 0.20 NTU, the percentage in the range between 0.21 NTU and 0.34 NTU, the percentage between 0.35 NTU and 0.54 NTU, and the percentage that equaled or exceeded 0.55 NTU. The percentage of filtered water turbidity results that exceed 1.0 NTU shall also be noted. In addition, the frequency of occurrence in which the filter was placed into service after backwashing and subsequently produced filtered water turbidity exceeding 0.5 NTU after a four hour ripening period (i.e. the turbidity did not fall to below 0.5 NTU within four hours of starting the filter) shall be noted. The time intervals used for determining turbidity values shall be the same for all data analyzed, and because continuous

turbidimeters are to be used to collect turbidity data, the intervals shall be between 5 and 15 minutes.

For systems treating ground water, turbidity results shall be analyzed to determine the percentage of turbidity data in the range of 0.50 NTU or lower, the percentage in the range of 0.51 NTU to 1.0 NTU, the percentage in the range between 1.1 NTU and 2.0 NTU, and the percentage exceeding 2.0 NTU.

## **11.0 TASK 3: OPERATING CONDITIONS AND TREATMENT EQUIPMENT PERFORMANCE**

### **11.1 Introduction**

Operating conditions shall be documented during each day of verification testing. This shall include descriptions of chemicals used for coagulation, pretreatment chemistry for coagulation, treatment processes used, and operating conditions. In addition, the performance of the water treatment equipment shall be documented, including rate of filter head loss gain, frequency and duration of filter cleaning, and need for cleaning of pretreatment clarifiers.

### **11.2 Objective**

The objective of this task is to accurately and fully document the operating conditions applied during treatment and the equipment performance. This task is intended to result in operational data describing the operation of the equipment, which can be used to develop cost estimates.

### **11.3 Work Plan**

A description of the testing equipment shall include:

- Complete description of each process, with data on volume and detention time of each process basin at rated flow;
- Data on each layer of the granular media filtering and support material, including:
  - Depth
  - Material type
  - Effective size
  - Uniformity coefficient;
- Manufacturer's data describing characteristics of membrane filter, precoat filter, cartridge filter, bag filter, or backwashable depth filter; and
- Location of each chemical or polymer addition point.

During verification testing, the following items shall be monitored, collected, recorded, or analyzed:

- Treatment equipment operating parameters for both pretreatment and filtration, including:
  - Pretreatment chemistry,

- Pre-oxidation operating parameters, if pre-oxidation is used,
  - Mixing and flocculation intensities,
  - Operating parameters for clarification ahead of filtration; rate of flow; and filtration rate, and
  - Process detention times.
- Filter head loss and backwashing data, cleaning data, precoating data, or data on changing filter cartridges or filter bags.
  - Chemical dosages for all chemicals used, including oxidants. If oxidation is used, oxidant dosage and residual oxidant shall be measured each time an arsenic sample is taken. In addition, the supplier and manufacturer of the coagulant chemical, the strength of solution for liquid coagulants, the specific gravity for liquid coagulants, and the chemical formula and percentage of impurities for dry coagulants shall be documented and included in the report of the testing. If ozone is used, the ozone system should be monitored according to Table 3 in the “The ETV Protocol for Inactivation of Microbiological Contaminants, Chapter 2, Test Plan for Ozone and Advanced Oxidation Processes”, except that frequency should be once per day for all parameters that are listed, on days when arsenic samples are not collected. Ozone monitoring shall be performed for parameters listed in Table 3 in the “The ETV Protocol for Inactivation of Microbiological Contaminants, Chapter 2, Test Plan for Ozone and Advanced Oxidation Processes” each time when an arsenic sample is obtained.
  - Quantities of filter aid used for precoating and body feed if precoat filtration equipment is used.
  - Electrical energy consumed by the treatment equipment or aggregate horsepower of all motors supplied with the equipment for estimating the maximum power consumption during operation. If ozonation is used in pre-oxidation, measurement of watt-hours of energy used is the recommended method for determination of energy usage. The energy use for the ozone system should be monitored according to Table 3 in the “The ETV Protocol for Inactivation of Microbiological Contaminants, Chapter 2, Test Plan for Ozone and Advanced Oxidation Processes”, except that the frequency should be once per day for the energy parameters that are listed.

#### **11.4 Schedule**

Table 4 presents the schedule for observing and recording coagulation and filtration equipment operating and performance data.

#### **11.5 Evaluation Criteria**

Where applicable, the data developed from this task will be compared to statements of performance objectives with respect to filter head loss, frequency and duration of filter cleaning or filter replacement, and the need for pretreatment clarifier cleaning.

If no relevant statement of performance objectives exists for each set of conditions employed in arsenic challenge testing, the results of operating and performance data shall be tabulated for inclusion in the verification report, and shall include:

- Average rate of flow for equipment, gallons/day;
- Average filtration rate, expressed in units appropriate for the filtration process used;
- Average run length, hours, and volume of water treated per filter run;
- Average daily chemical usage and cost factors for treatment chemicals, including filter aid for precoat filters, if used;
- Average daily energy cost factors;
- Average daily wash water production, if appropriate;
- Average daily sludge or floated solids production, and;
- Cleaning efficiency for membrane filters as described in Task 2 of the ETV Membrane Filtration Test Plan for the Removal of Microbiological and Particulate Contaminants, if applicable.

## **12.0 TASK 4: ARSENIC REMOVAL**

### **12.1 Introduction**

Arsenic removal may be a primary purpose of coagulation and filtration of some surface and ground waters. Consequently, the effectiveness of coagulation and filtration treatment processes for arsenic removal will be evaluated in this task. Additionally, turbidity removal is needed to ensure that water quality goals are met when treating surface waters. Therefore, assessment of treatment efficacy will be made on the basis of turbidity measurements (as described in Task 3) and arsenic removal for surface water treatment. For ground water treatment, assessment of treatment efficacy will be made on the basis of arsenic removal.

### **12.2 Experimental Objective**

The objective of this task is to evaluate arsenic removal during verification testing by measuring arsenic naturally present in the feed water or by spiking the feed water with arsenic in the treated water.

### **12.3 Work Plan**

Task 4 shall be carried out during the verification testing runs conducted in Task 1. The treatment equipment shall be operated using the chemical pretreatment conditions that provide effective clarification (if used) and filtration.

Evaluation of arsenic removal shall be performed by analyzing arsenic in the feed and filtered waters. If arsenic spike testing is required, the appropriate arsenic species [either arsenate (V) or arsenite (III)] will be added to the feedwater.

A minimum of 48 hours of operation involving collection of 11 or more arsenic samples shall be conducted to provide statistically verifiable arsenic removal data for each condition of coagulant chemical type and dosage, coagulation pH, feed water arsenic species, and feed water arsenic concentration tested.

### **12.3.1 Background Arsenic Levels**

If sufficient arsenic concentration is naturally present in the feed water to meet the manufacturer's stated operating range for arsenic removal, the treatment equipment shall be operated as usual in verification testing runs, and sampling shall be done as stipulated in the analytical schedule.

### **12.3.2 Spiked Arsenic**

Spiked arsenic shall be used in concentrations sufficient to permit the most-stressed operations for the manufacturer's equipment, following the recommended guidelines:

- Arsenic spiking shall begin at start-up of the treatment equipment.
- Arsenic feed solution will be prepared by diluting the arsenic into dilution water that is distilled or deionized and oxidant free.
- To spike arsenic (III), use commercially-prepared arsenic trioxide. (In cold water, at 2°C, the solubility of this chemical is about 1.2 g/100 g water.)
- To spike arsenic (V), use commercially-prepared arsenic pentoxide.
- Feed reservoir for the arsenic spike solution shall be made of chemically inert material (i.e., not reactive or adsorbable to the arsenic).
- The reservoir will be mixed continuously throughout the experiment.
- The arsenic spike solution will be fed using an adjustable rate chemical feed pump.
- Use an in-line static mixer to mix this solution into the feedwater.
- Arsenic samples of at least 250 mL shall be collected in bottles prepared for holding such samples.

If testing with Arsenic (III) is contemplated, manufacturers and FTOs need to be aware of potential difficulties in preventing conversion of As (III) to As (V) as the spiking solution is held in its storage container. Further conversion to the higher valence state could occur during passage of spiked water through the equipment. Several of the arsenic studies referenced in this TSTP have shown that As (V) removal by coagulation and filtration is much more effective than As (III) removal. Thus, a preferred approach to arsenic

treatment may involve pre-oxidation to convert all arsenic to As (V) so the most effective results will be attained. If pre-oxidation is done, the conditions need to be documented.

## **12.4 Analytical Schedule**

Turbidity in feed water samples may be measured on a batch or a continuous basis. For facilities treating surface waters, if batch measurements are used, they shall be performed every six hours during each working day in the verification testing. Filtered water analysis shall be conducted using continuous flow turbidimeters equipped with recording capability so data can be collected on a 24-hour-per-day basis during verification testing.

Chemistry samples shall be collected from the plant influent (feed water after spiking, if arsenic is spiked), clarifier effluent if a clarification step is employed ahead of filtration, and the filter effluent. Samples shall not be collected until the treatment plant has been in operation for a total of three (3) theoretical detention times (the theoretical detention time is the volume of water held in the treatment equipment, divided by the rate of flow) as measured through the pretreatment process up to the filter. For arsenic sampling purposes, the time of operation when three pretreatment detention times have elapsed shall be considered time zero. Arsenic samples shall be collected at time zero and at 1, 3, and 6 hours past time zero. Thereafter, arsenic samples shall be collected once every 6 hours until the end of the filter run or until the filter run has lasted 48 hours from time zero. This would result in collection of 11 sets of arsenic samples in a 48-hour filter run. Because four sets of arsenic samples are to be collected during the first 6 hours of a filter run, conducting more than one filter run during the 48 hour period required for a given set of treatment conditions would result in collection of more than 11 sets of arsenic samples. During each sampling event, one 250-mL sample will be collected at each sampling location. The exact time of sampling will be recorded so turbidity measurements can be determined at the time of sampling. When Task 4 is carried out, if pre-oxidation is done, the pre-oxidant dosage and the pre-oxidant residuals are to be determined at time zero and at 6-hour intervals through the 48-hour time period required for this task. The total concentration of iron or aluminum acting as a coagulant to co-precipitate arsenic shall be determined in each feed water sample and filtered water sample for which the arsenic concentration is determined.

For filtration process equipment other than granular media filters, eleven (11) sets of feed water and filtered water arsenic samples shall be collected, but the timing for collection of those samples shall be as indicated in the PSTP, specific to the filtration process equipment being evaluated, with reference to the timing for sample collection during microbial contaminant challenges. Regardless of the wording related to the number of microbiological or microbe surrogate challenge samples to be collected, no fewer than eleven sets of arsenic samples shall be collected.

The FTO shall then submit collected water samples to a state or EPA-accredited analytical laboratory for arsenic testing. The laboratory shall have a minimum detection limit for arsenic of 2 µg/L.

## **12.5 Evaluation Criteria**

Performance evaluation shall be conducted in a number of ways, depending on the types of data collected during testing. Performance of coagulation and filtration equipment shall be evaluated in the context of the manufacturer's statement of performance objectives with respect to arsenic removal and the filtered water turbidity goals, if surface water was treated. For arsenic removal by coagulation and filtration, the following information shall be provided:

- Valence of the arsenic being treated by coagulation and filtration, i.e. As (III) or As (V);
- pH of coagulated water;
- Coagulant chemical used;
- Coagulant dosage or concentration of coagulant such as iron naturally present in the feed water; and
- Concentration of oxidant added, if an oxidant is used.

An example of a statement of performance objectives for arsenic removal might be, "Coagulation and filtration in the pH range of 7.0 to 8.0 can reduce arsenate [Arsenic (V)] concentration by 90 percent when the initial arsenic concentration is in the range of 20 to 100 µg/L and a 30 mg/L dose of ferric sulfate is used for coagulation." To provide data to verify such a performance statement, testing would have to be done at pH 7.0 for feed water with arsenic at 20 µg/L and with arsenic at 100 µg/L. Testing at both arsenic concentrations also would be required at pH 8.0. If a statement of performance objectives specifies the type of coagulant and the dosage that is effective, both the coagulant type and dosage would also be required to be used for all conditions tested.

## **13.0 TASK 5: DATA MANAGEMENT**

### **13.1 Introduction**

The data management system used in the verification testing program shall involve the use of computer spreadsheet software and manual recording of operational parameters for the water treatment equipment on a daily basis.

### **13.2 Experimental Objectives**

The objective of this task is to establish a viable structure for the recording and transmission of field testing data such that the FTO provides sufficient and reliable operational data for verification purposes. A second objective is to develop a statistical analysis of the data, as described in "Protocol for Equipment Verification Testing for Arsenic Removal."

## 13.3 Work Plan

### 13.3.1 Data Handling

The following protocol has been developed for data handling and data verification by the FTO. Where possible, a Supervisory Control and Data Acquisition (SCADA) system should be used for automatic entry of testing data into computer databases.

- Specific parcels of the computer databases for operational and water quality parameters should be downloaded by manual importation into Excel (or similar spreadsheet software) as a comma delimited file.
- Specific database parcels will be identified based on discrete time spans and monitoring parameters.
- The data will be manipulated into a convenient framework to allow analysis of coagulation and filtration equipment operation in a spreadsheet form.
- Backup of the computer databases to diskette should be performed on a monthly basis at a minimum.

In the case when a SCADA system is not available:

- Field testing operators will record data and calculations by hand in laboratory notebooks. (Daily measurements will be recorded on specially-prepared data log sheets as appropriate.)
- Laboratory notebook will contain carbon copies of each page (to ease referencing the original data and offer protection of the original record of results).
- Original notebooks will be stored on-site; the carbon copy sheets will be forwarded to the project engineer of the FTO at least once per week.
- Operating logs shall include a description of the process equipment (description of test runs, names of visitors, description of any problems or issues, etc.); such descriptions shall be provided in addition to experimental calculations and other items.

Spreadsheets:

- The data for the project will be recorded in custom-designed spreadsheets.
- The spreadsheets will be capable of storing and manipulating each monitored water quality and operational parameter from each task, sampling location, and sampling time.



- All data from the laboratory notebooks and data log sheets will be entered into the appropriate spreadsheet.
- Data entry will be conducted on-site by the designated field testing operators, with all recorded calculations checked at this time.
- Following data entry, the spreadsheet will be printed out and the printout will be checked against the handwritten data sheet.
- Any corrections will be noted on the hard-copies and corrected on the screen, and a corrected version of the spreadsheet will be printed out.
- Each step of the verification process will be initialed by the field testing operator or engineer performing the entry or verification step.

#### Data tracking:

- Each experiment (e.g., each filtration test run) will be assigned a run number which will then be linked to the data from that experiment through each data entry and analysis step.
- Data will be tracked by use of the same system of run numbers as samples are collected and sent to State or EPA-accredited analytical laboratories.
- Data from the analytical laboratories will be received and reviewed by the FTO.
- These data will be entered into the data spreadsheets, corrected, and checked in the same manner as the field data.

### **13.3.2 Statistical Analysis**

Arsenic data developed from grab samples collected during filter runs according to the analytical schedule in Task 4 of this TSTP shall be analyzed for statistical uncertainty. The FTO shall calculate 95% confidence intervals for the arsenic data obtained during verification testing as described in Chapter 1 of the “Protocol for Equipment Verification Testing for Arsenic Removal.” A separate statistical analysis shall be carried out for each testing condition for which the required 11 or more sets of arsenic samples were collected and analyzed.

The statistics developed will be helpful in demonstrating the degree of reliability with which the water treatment equipment can attain quality goals under the treatment conditions tested. The results of the statistical analysis also shall be used to determine if the performance of the equipment was equal to or better than that given in the statement of performance objectives.

## **14.0 TASK 6: Quality Assurance/Quality Control**

### **14.1 Introduction**

QA/QC of the operation of the coagulation and filtration equipment and the measured water quality parameters shall be maintained during the verification testing program.

### **14.2 Experimental Objectives**

The objective of this task is to maintain strict QA/QC methods and procedures during the equipment verification testing program. When specific items of equipment or instruments are used, the objective is to maintain the operation of the equipment or instructions within the ranges specified by the manufacturer or by *Standard Methods*. Maintenance of strict QA/QC procedures is important, in that if a question arises when analyzing or interpreting data collected for a given experiment, it will be possible to confirm exact conditions at the time of testing.

### **14.3 Work Plan**

Equipment flow rates and associated signals should be documented and recorded on a routine basis. A routine daily walk-through during testing will check that each piece of equipment or instrumentation is operating properly. Particular care will be taken to confirm the water and chemicals flow rates to ensure that the chemical feed concentrations are correct. In-line monitoring equipment, such as flow meters and turbidimeters, will be checked to confirm that the readout matches with the actual measurement (i.e. flow rate, turbidity) and that the signal being recorded is correct. The items listed are in addition to any specified checks outlined in the analytical methods.

#### **14.3.1 Daily QA/QC Checks**

- Chemical feed pump (if used) flow rates (checked volumetrically over a specific period of time to confirm instrument reading);
- In-line turbidimeters flow rates (checked volumetrically over a specific period of time to confirm instrument reading); and
- In-line turbidimeters readings checked against a properly calibrated bench model.

#### **14.3.2 QA/QC Checks Performed Every Two Weeks**

- In-line flow meters/rotameters (clean equipment to remove any debris or biological buildup and check flow volumetrically over a specific period of time to confirm instrument reading).

#### **14.3.3 QA/QC Checks for Each Test Period**

- In-line turbidimeters (clean out reservoirs, if necessary, and recalibrate);
- Differential pressure transmitters (check gauge readings and electrical signal using a pressure meter); and

- Tubing (check condition of all tubing and connections, replace if necessary).

## 14.4 On-Site Analytical Methods

The analytical methods utilized in this study for on-site monitoring of raw water and treated water quality are described in the section below. If new methods are published and approved or current methods updated, the most current methods shall be used. In-line equipment is recommended for its ease of operation and because it limits the introduction of error and the variability of analytical results generated by inconsistent sampling techniques. In-line equipment is recommended for measurement of turbidity and particle counting for feed water, and is required for measurement of turbidity and particle counting for filtered water.

### 14.4.1 pH

pH analysis shall be performed according to *Standard Method 4500-H<sup>+</sup>* or EPA Methods 150.1 and 150.2. A three-point calibration of the pH meter shall be performed once per day when the instrument is in use. Certified pH buffers in the expected range shall be used. The pH probe shall be stored in the appropriate solution defined in the instrument manual. Transport of carbon dioxide across the air-water interface can confound pH measurement in poorly buffered waters. If this is a problem, pH measurement in a confined vessel is recommended to minimize the effects of carbon dioxide loss to the atmosphere.

### 14.4.2 Turbidity

Turbidity analyses shall be performed according to *Standard Method 2130 B* or EPA Method 180.1 with either a bench-top or in-line turbidimeter. In-line turbidimeters shall be used for measurement of turbidity in the filtrate waters, and either an in-line or bench-top may be used for measurement of the feedwater.

During each verification testing period, the bench-top and in-line turbidimeters will be left on continuously. Once each turbidity measurement is complete, the unit will be switched back to its lowest setting. All glassware used for turbidity measurements will be cleaned and handled using lint-free tissues to prevent scratching. Sample vials will be stored inverted to prevent deposits from forming on the bottom surface of the cell.

The FTO shall document any problems experienced with the monitoring turbidity instruments, and shall also document any subsequent modifications or enhancements made to monitoring equipment.

**14.4.2.1 Bench-Top Turbidimeters.** Grab samples shall be analyzed using a bench-top turbidimeter. Readings from this instrument will serve as reference measurements throughout the study. The bench-top turbidimeter shall be calibrated within the expected range of sample measurements at the beginning of equipment operation and on a weekly basis using primary turbidity standards of 0.1, 0.5, and 3.0 NTU. Secondary turbidity standards shall be obtained and checked against the primary standards. Secondary

standards shall be used on a daily basis to check calibration of the turbidimeter and to recalibrate when more than one turbidity range is used.

The method for collecting grab samples will consist of running a slow, steady stream from the sample tap, triple-rinsing a dedicated sample beaker in this stream, allowing the sample to flow down the side of the beaker to minimize bubble entrainment, double-rinsing the sample vial with the sample, carefully pouring from the beaker down the side of the sample vial, wiping the sample vial clean, inserting the sample vial into the turbidimeter, and recording the measured turbidity.

For the case of cold water samples that cause the vial to fog preventing accurate readings, allow the vial to warm up by submersing partially into a warm water bath for approximately 30 seconds.

**14.4.2.2 In-Line Turbidimeters.** In-line turbidimeters are required for filtered water monitoring during verification testing and must be calibrated and maintained as specified in the manufacturer's operation and maintenance manual. It will be necessary to check the in-line readings using a bench-top turbidimeter at least daily; although the mechanism of analysis is not identical between the two instruments, the readings should be comparable. Should these readings suggest inaccurate readings, then all in-line turbidimeters should be recalibrated. In addition to calibration, periodic cleaning of the lens should be conducted, using lint-free paper, to prevent any particle or microbiological build-up that could produce inaccurate readings. Periodic check of the sample flow rate should also be performed using a volumetric measurement. Instrument bulbs should be replaced on an as-needed basis. The LED readout shall be checked that it matches the data recorded on the data acquisition system, if the latter is employed.

### **14.4.3 Temperature**

Readings for temperature shall be conducted in accordance with *Standard Method 2550*. Raw water temperatures should be obtained at least once daily. The thermometer shall have a scale marked for every 0.1°C, as a minimum, and should be calibrated weekly against a precision thermometer certified by the National Institute of Standards and Technology (NIST). (A thermometer having a range of -1°C to +51°C, subdivided in 0.1° increments, would be appropriate for this work.)

### **14.4.4 True Color**

True color shall be measured with a spectrophotometer at 455 nm, using a Hach Company adaptation of the *Standard Method 2120 B* procedure. Samples should be collected in clean plastic or glass bottles and analyzed as soon after collection as possible. If samples can not be analyzed immediately, they should be stored at 4°C for up to 24 hours, and then warmed to room temperature before analysis. The filtration system described in *Standard Method 2120 C* should be used, and results should be expressed in terms of PtCo color units.

#### **14.4.5 Chlorine Residual**

Because free chlorine in aqueous solutions is unstable, the free chlorine concentration in treated water samples will decrease rapidly. Exposure to sunlight or other strong light, or agitation, will accelerate free chlorine loss. Therefore, analysis of free and total chlorine samples shall begin immediately after sampling, and excessive light and agitation shall be avoided. Samples to be analyzed for free or total chlorine shall not be stored prior to analysis.

Glassware to be used for chlorine analyses shall be chlorine demand free. Chlorine demand free glassware will be prepared by soaking glassware in a 50 mg/L chlorine bath for a period of 24 hours. At the end of this time, all glassware will be rinsed three times with organic-free water that has a TOC concentration of less than 0.2 mg/L. Glassware will then be dried at room temperature for a period of 24 hours. During the drying process, bottle openings will be covered with aluminum foil to prevent contamination.

The method for collecting samples for chlorine analyses shall consist of the following procedure: running a slow, steady stream from the sample tap, triple-rinsing a chlorine demand free sample beaker in this stream; allowing the sample to flow down the side of the beaker to minimize agitation; performing the free and total chlorine analyses; and recording the measured chlorine concentrations.

#### **14.4.6 Chlorine Dioxide Residual**

Similar to chlorine, chlorine dioxide in aqueous solutions is unstable. Exposure to sunlight or other strong light, or agitation, will accelerate chlorine dioxide loss. Therefore, analysis of chlorine dioxide samples shall begin immediately after sampling, and excessive light and agitation shall be avoided. Samples to be analyzed for chlorine dioxide shall not be stored prior to analysis. Glassware for chlorine dioxide analyses shall be chlorine demand free, as described above in Section 14.4.5. The method for collecting samples for chlorine dioxide residual shall be identical to that described above for chlorine residual.

#### **14.4.7 Dissolved Ozone and Gas Phase Ozone**

For dissolved and gas phase ozone analyses, refer to the “The ETV Protocol for Inactivation of Microbiological Contaminants, Chapter 2, Test Plan for Ozone and Advanced Oxidation Processes” section 14.4.7 for dissolved ozone measurement and section 14.4.8 for gas phase ozone analysis.

### **14.5 Chemical and Biological Samples Shipped Off-Site for Analyses**

#### **14.5.1 Total Organic Carbon and UV<sub>254</sub> Absorbance**

Samples for analysis of TOC and UV<sub>254</sub> absorbance shall be collected in glass bottles supplied by the state-certified or third party- or EPA- accredited laboratory and shipped

at 4°C to the analytical laboratory. These samples shall be preserved, held, and shipped in accordance with *Standard Method 5010B*. Storage time before analysis shall be minimized, according to *Standard Methods*.

#### **14.5.2 Arsenic**

Laboratory analyses for arsenic shall be performed in accordance with EPA Method 200.8. These analyses are the most critical for the entire ETV procedure. When arsenic species are to be analyzed, the samples shall be collected and preserved in accordance with the Protocol for Arsenic Speciation developed by Battelle for the EPA, as found in Appendix A of this protocol. EPA Method 200.8 has been specified because of the need to achieve low detection limits (0.002 to 0.004 mg/L) with good accuracy and precision for this verification test. Other EPA approved drinking water methods that can achieve these low laboratory reporting limits with comparable accuracy and precision may be proposed by the FTO. Please note when using this method that ultra-pure (optimum) grade sulfuric acid must be used (not reagent grade) to avoid the trace amounts of arsenic that can be present in reagent grade sulfuric acid.

#### **14.5.3 Other Inorganic Samples**

Inorganic chemical samples, including arsenic, alkalinity, hardness, aluminum, iron, and manganese, shall be collected, preserved, shipped, and held in accordance with *Standard Method 3010B*, paying particular attention to the sources of contamination as outlined in *Standard Method 3010C*. The samples shall be refrigerated at approximately 4°C immediately upon collection, shipped in a cooler, and maintained at a temperature of approximately 4°C during shipment. Samples shall be processed for analysis by a state-certified or third party- or EPA- accredited laboratory within 24 hours of collection. The laboratory shall keep the samples at approximately 4°C until initiation of analysis.

#### **14.5.4 Algae**

Algae samples shall be preserved with Lugol's solution after collection, stored and shipped in a cooler at a temperature of approximately 4°C, and held at that temperature range until counted.

### **15.0 OPERATIONS & MAINTENANCE**

The FTO shall obtain the manufacturer-supplied Operations and Maintenance (O&M) manual to evaluate the instructions and procedures for their applicability during the verification testing period. The following are recommendations for criteria for O&M manuals for equipment employing coagulation and filtration.

Most of the recommendations in this section are for equipment employing granular media filtration. For arsenic removal equipment using other filtration processes, refer to the TSTP developed for the filtration process being used as a source of guidance on other O&M aspects to consider.

## **15.1 Maintenance**

The manufacturer should provide readily understood information on the recommended or required maintenance schedule for each piece of operating equipment such as:

- Pumps;
- Valves;
- Pressure gauges;
- Flow meters;
- Chemical feeders;
- Mixers;
- Motors;
- Instruments, such as continuous pH monitors or turbidimeters;
- Water meters, if provided; and
- Ozonation system, if provided (per requirements in section 15.1 of “The ETV Protocol for Inactivation of Microbiological Contaminants, Chapter 2, Test Plan for Ozone and Advanced Oxidation Processes”).

The manufacturer should provide readily understood information on the recommended or required maintenance for non-mechanical or non-electrical equipment such as:

- Tanks and basins;
- In-line static mixers; and
- Filter vessels.

## **15.2 Operation**

The manufacturer should provide readily understood recommendations for procedures related to proper operation of the equipment. Among the operating aspects that should be discussed are:

Pre-oxidant generation/feed:

- Measurement of pre-oxidant concentration generated;
- Measurement of pre-oxidant concentration fed into treatment equipment; and
- Ozonation system, if provided (per requirements in section 15.2 of “The ETV Protocol for Inactivation of Microbiological Contaminants, Chapter 2, Test Plan for Ozone and Advanced Oxidation Processes”).

Chemical feeders:

- Calibration check;
- Settings and adjustments -- how they should be made; and
- Dilution of chemicals and polymers -- proper procedures.

Mixers and flocculators:

- Purpose and
- Changing intensity (RPM), if available.

Filtration:

- Control of filtration flow and rate and
- Observation and measurement of head loss during filter run.

Filter backwashing, if applicable:

- End of filter run;
- Use of auxiliary water scour (surface wash) or air scour;
- Start of backwash;
- Appropriate backwash rates;
- Conclusion of filter backwashing; and
- Return of filter to service.

Filter cleaning for membrane filters, if applicable or for backwashable depth filters, if applicable.

Filter cleaning and precoating for precoat filters, if applicable.

Changing filter cartridges or filter bags, if applicable.

Monitoring and observing operation:

- Observation of floc;
- Pretreated water turbidity, if appropriate;
- Filtered water turbidity;
- Filter head loss;
- What to do if turbidity breakthrough occurs; and
- Measuring and controlling pH of coagulated water.

Coagulant dose selection:

It is strongly recommend that manufacturer include a copy of AWWA's Manual M37, "Operational Control of Coagulation and Filtration Processes" with each coagulation and filtration package plant, as an AWWA committee of experts has prepared an excellent manual that would be very helpful to plant operators.

The manufacturer should provide a troubleshooting guide; a simple check-list of what to do for a variety of problems including:

- No raw water (feed water) flow to plant;



- Can't control rate of flow of water through equipment;
- No chemical feed;
- Loss of pre-oxidant feed;
- Calibration and maintenance of in-line pH monitoring instruments, problems of erratic pH or drifting pH readings;
- Mixer or flocculator will not operate (won't rotate);
- Filter can't be backwashed or backwash rate of flow can't change;
- No reading on turbidimeter or streaming current monitor;
- Automatic operation (if provided) not functioning;
- Filtered water turbidity too high;
- Filter head loss builds up excessively rapidly;
- No head loss readings;
- Valve stuck or won't operate; and
- No electric power.

The following are recommendations regarding operability aspects of equipment employing coagulation and filtration. These aspects of plant operation should be considered, if possible, in reviews of historical data and should also be included to the extent practical in verification reports.

During verification testing and during compilation of historical equipment operating data, attention shall be given to equipment operability aspects. Among the factors that should be considered are:

- Fluctuation of chemical feed rate from desired value -- the time interval at which re-setting is needed (i.e., how long can feed pumps hold on a set value for the feed rate?).
- Ability to maintain desired pre-oxidant feed rate.
- Presence of devices to aid the operator with chemical dosage selection:
  - streaming current monitor provided?
  - influent and filtered water continuous turbidimeters provided?
  - in-line pH meter provided?
- Can backwash be done automatically?
- If automatic backwash provided, could it be initiated by:
  - reaching a set value for head loss?
  - reaching a set value for filtered water turbidity?
- Does remote notification to operator occur when backwash happens?
- Can operator observe filter backwash?
- How can plant operator check on condition and depth of filter media?

- Can flocculation energy be varied?
- Does plant have multiple feed points for chemicals:
  - for pH adjustment?
  - for coagulant chemical feed?
  - for polymer feed?
  - for oxidants?
- Is head loss measurement provided?
- Is rate of flow of raw water measured?
- Is chemical feed paced with raw water flow?
- Can coagulation pH be maintained automatically if raw water flow changes?
- Is backwash rate of flow measured and variable?
- Is backwash duration (time) variable?

Does the equipment have sensors or monitoring equipment that can detect an equipment malfunction, unsatisfactory treated water quality, or operating conditions that exceed allowable limits, and if so, during such situations can the equipment be automatically shut down? Upon automatic shutdown, can a means of operator notification be provided, if the operator is not present on the site where the equipment is located?

Both the reviews of historical data and the reports on verification testing should address the above questions in the written reports. The issues of operability should be dealt with in the portion of the reports that are written in response to Task 3: Operating Conditions and Treatment Equipment Performance, in this TSTP.

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**Table 1. Generic Schedule for Verification Testing**

A period of initial operations is required for all filtration process equipment. This initial operations testing may require from 1 to 6 weeks.

<b>Filtration Process</b>	<b>Required Duration of Verification Testing Period</b>
Granular Media	320 hours
Precoat Filtration	320 hours
Bag Filters, Cartridge Filters, Backwashable Depth Filters	320 hours minimum; however verification testing must be performed for a period of time sufficiently long to attain one change/replacement of bag or cartridge. If such a change has not occurred at 29 days due to lack of terminal head loss development, the bag/cartridge shall be replaced and the equipment shall be operated for at least 24 hours longer, with the total operating time to be at least 30 days
Membrane Filtration Equipment	30 days

<b>Table 2. Water Quality Sampling and Measurement Schedule</b>	
<b>Parameter</b>	<b>Minimum Frequency</b>
Temperature	Daily
pH <sup>1</sup>	Once per day during runs with no arsenic sampling. Measure pH of coagulated water each time arsenic samples are collected.
Total Alkalinity	Daily
Hardness	Weekly <sup>2</sup>
Total Organic Carbon	Weekly <sup>2</sup>
UV254 Absorbance	Weekly <sup>2</sup>
Turbidity	Daily at bench to check continuous turbidimeters
Aluminum	Weekly <sup>2,3</sup>
Iron	Weekly <sup>2,3</sup>
Manganese	Weekly <sup>2</sup> if present in concentration of 0.05 mg/L or greater
Total Suspended Solids in backwash water	See Task 4
Arsenic	See Task 4
Sulfate	Weekly
Dissolved Oxygen in feedwater	Daily
Algae, number and species	Weekly or once during each set of treatment conditions for which arsenic sampling is done
True Color	Weekly <sup>2</sup>
Dosage of pre-oxidation chemical and pre-oxidation chemical residual in filtered water	Only in Task 4, every 6 hours beginning at time zero

Sampling points: feed water, clarified water (if applicable) and filtered water.

During arsenic challenge testing, collection of weekly and daily samples shall be coordinated with arsenic sampling so other water quality data can be related to arsenic results.

<sup>1</sup> For pH samples, filtered water pH values are valid only if no pH adjusting chemicals are added after coagulation. The pH of filtered water is intended to represent the pH of coagulation.

<sup>2</sup> When used as the coagulant to co-precipitate arsenic, measure daily when arsenic samples are not taken on a given day.

<sup>3</sup> When used as the coagulant to co-precipitate arsenic, measure influent to filter and filtered water each time arsenic is sampled.

<b>Table 3. Analytical Methods</b>			
<b>Parameter</b>	<b>Facility</b>	<b>Standard Methods<sup>1</sup> number or Other Method Reference</b>	<b>EPA Method<sup>2</sup></b>
Temperature	On-Site	2550	
pH	On-Site	4500-H <sup>+</sup> B	150.1, 150.2
Total Alkalinity	On-Site	2320 B	
Total Hardness	Lab or On-Site <sup>3</sup>	2340 C	
Total Organic Carbon	Lab	5310 C	
UV <sub>254</sub> absorbance	Lab	5910 B	
Turbidity	On-Site	2130 B	180.1
Aluminum	Lab	3120 B	200.7, 200.8, 200.9
Iron	Lab	3120 B	200.7, 200.9
Manganese	Lab	3120 B	200.7, 200.8, 200.9
Total Suspended Solids in backwash water	Lab	2450 D	
Algae, number and species	Lab	10200 and 10900	
Sulfate	Lab	4110 B, 4500-SO <sub>4</sub> <sup>2-</sup> C, D, E, & F	300.0, 375.2
Dissolved Oxygen	On-Site	4500-O C or G	
True Color	On-Site	2120 B (Hach Company modification of SM 2120 measured in spectrophotometer at 455 nm)	
Arsenic	Lab		200.8
Arsenic Speciation	Lab		Battelle Speciation Method and Arsenic by 200.8 <sup>4</sup>
Pre-oxidants: Ozone Residual Chlorine Chlorine Dioxide Potassium Permanganate (if used to oxidize Arsenic III)	On-Site On-Site On-Site Lab	4500-O <sub>3</sub> B; HACH Indigo Blue Method <sup>5</sup> 4500-Cl 4500-ClO <sub>2</sub> 3111	
TCLP	Lab		1311 and metals analysis by SW-846 6010 and 7470a <sup>6</sup>
California Waste Extraction Test (WET)	Lab		Special CA method and metals analysis by SW- 846 6010 and 7470a <sup>6</sup>

<sup>1</sup> Standard Methods Source: 20th Edition of *Standard Methods for the Examination of Water and Wastewater*, 1999, AWWA.

<sup>2</sup> EPA Methods Source: EPA Office of Ground Water and Drinking Water. EPA Methods are available from the National Technical Information Service (NTIS).

<sup>3</sup> On-Site or at Laboratory, must meet short holding time requirements.

<sup>4</sup> Speciation Method developed by Battelle for EPA (see Appendix A).

<sup>5</sup> Dissolved ozone residual measurements can also be from a properly calibrated and installed dissolved ozone monitor.

<sup>6</sup> Metals analyses shall include As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Se, Ag, Zn.

<b>Table 4. Equipment Operating Data</b>	
<b>Operating Data</b>	<b>Action</b>
Chemicals Used	Record on a daily basis: type; supplier; commercial strength (e.g. as percent Fe or Al, specific gravity of liquid coagulants or percent purity and chemical formula of dry coagulants); and dilution for stock solution to be fed (if diluted).
Chemical Type, Feed Volume and Dosage	Check and record each 2 hours. Refill as needed, note volumes and times of refill. Maintain all calculations on coagulant chemical solution preparation and all data on coagulant chemicals as purchased from supplier or chemical manufacturer. Calculate the chemical dosage for each filter run in which arsenic challenge testing was carried out.
Ozonation System	See Section 15.2 and Table 3 of “The ETV Protocol for Inactivation of Microbiological Contaminants, Chapter 2, Test Plan for Ozone and Advanced Oxidation Processes”
RPM of Rapid Mix and Flocculator	Check once/day and record
Feedwater Flow and Filter Flow	Check and record each two hours Adjust when flow >10% above or below goal Record flows before and after adjustment.
Filter Head Loss	Record initial clean bed total head loss at start of filter run Record total head loss every two hours. Record terminal head loss at end of filter run.
Filtered Water Production	Record gallons of water produced per square foot of filter area, for each filter run. [This figure is the product of filtration rate (gpm/sf) and length of filter run in minutes for a filter run performed at constant rate.]
Filter Backwash	Record time and duration of each filter backwashing. Record water volume used to wash filter.
Sludge Production	If sludge is drawn off, record volume of sludge.
Suspended solids in washwater	Determine suspended solids in washwater for each set of arsenic removal testing conditions.
Clarifier/flocculator or other similar process ahead of filter	If clarifier/flocculator is backwashed separately from backwashing of filter, record the time of every backwash for this process, and volume of water used.
DAF flotote removal	Record frequency of flotote removal action each day.



<b>Table 4. Equipment Operating Data (continued)</b>	
<b>Operating Data</b>	<b>Action</b>
DAF recycle flow	Record recycle water flow rate each 8 hours.
DAF saturator pressure	Record DAF saturator vessel pressure each 8 hours.
Electric Power	Record meter reading once per day
Hours operated per day	Record in logbook at end of day or at beginning of first shift on the following workday.

All parameters will be checked only during times when the equipment is staffed.

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## Appendix A

### Protocol for Arsenic Speciation



## PROTOCOL FOR ARSENIC SPECIATION

The following text presents the protocol to be used for arsenic speciation sampling and analysis during this project.

### 1.0 Scope and Application

Arsenic occurs in natural water in both the organic and inorganic forms. However, inorganic arsenic is predominant in natural water and is the most likely form of arsenic to exist at concentrations that cause regulatory concerns (Edwards et al., 1997). Inorganic arsenic is normally found in water supplies as an anion with acid characteristics in the trivalent [arsenite or As (III)] and pentavalent [arsenate or As (V)] forms. The valence is significant because most arsenic treatment technologies are more effective for the removal of arsenate than for arsenite.

Although total arsenic concentrations can be effectively preserved in field samples, the present status of preserving inorganic arsenic species in field samples is inconclusive. Preservation of total arsenic is accomplished by acidifying the sample to  $\text{pH} < 2$  in the field. However, a high level of ambiguity exists when acids such as nitric acid ( $\text{HNO}_3$ ) or hydrochloric acid ( $\text{HCl}$ ) are used to preserve inorganic species of arsenic. Interconversion of As (III) and As (V) in samples preserved with 0.05 *N*  $\text{HCl}$  has been reported to occur within one day (Andreae, 1977). Another laboratory study conducted by Eaton et al. (1997) examined preservation of arsenic using ascorbic acid and  $\text{HCl}$ . This study concluded that there were no effective methods for preservation of As (III) and As (V) in water samples. Some researchers have used freezing of samples as a means of preserving the inorganic species of arsenic. However, freezing is not a cost-effective or practical method for field sampling.

Since the present status of preserving arsenic species indicates that there are no completely effective preservation methods, field speciation is required. Research by Clifford et al. (1983), Ficklin (1983), and Edwards et al. (1997) indicate that the use of an anion exchange resin column is an accurate and cost-effective field method for arsenic speciation. As (III) and As (V) recovery was shown to be consistently above 95% using an anion exchange column (Edwards et al., 1997). Therefore, the decision was made to utilize a field speciation technique similar to that used by Edwards et al. (1997).

The field speciation technique described in the following sections uses 0.45- $\mu$ m pore size filters to remove "particulate" arsenic. Research done by Edwards et al. (1997) also using 0.45- $\mu$ m pore size filters indicates that particulate arsenic may not be completely removed by this pore size filter. Therefore, the particulate arsenic found using a 0.45- $\mu$ m pore size filter should be considered the lower bound for arsenic particulate.

The only laboratory analysis required using the field speciation technique is total arsenic. Inductively coupled plasma-mass spectrometry (ICP-MS) was chosen as the method for total arsenic analysis due to its low method detection limit (MDL), proven effectiveness, and relatively low cost.

## 2.0 Method Summary

The field speciation method described in the subsequent sections utilizes an anion exchange resin column to separate the soluble arsenic species, As (V) and As (III). The soluble portion of the sample is obtained by passing the sample through a 0.45- $\mu$ m pore size filter. After filtration, the sample is acidified using 0.5 mL of ultra-pure sulfuric acid per L of sample (0.05% [volume/volume]) to lower the sample pH value to about 2. At this pH range, As (III) will be completely protonated as  $\text{H}_3\text{AsO}_3$  (see Figure A-1) and As (V) will be present in both the ionic form (i.e.,  $\text{H}_2\text{AsO}_4^-$ ) and protonated form (i.e.,  $\text{H}_3\text{AsO}_4$ ) (see Figure A-2). As the acidified sample is run through the column, the resin retains the As (V) (Note that the resin will retain only  $\text{H}_2\text{AsO}_4^-$  and that  $\text{H}_3\text{AsO}_4$ , when passing through the column, will be ionized to  $\text{H}_2\text{AsO}_4^-$  due to elevated pH values in the column caused by the buffer capacity of acetate exchanged from the resin) and the As (III) (i.e.,  $\text{H}_3\text{AsO}_3$ ) passes through the column. The acidified sample and the resin-treated sample are analyzed separately for total arsenic using ICP-MS. As (III) concentration is reflected by the total arsenic concentration of the resin-treated sample. As (V) concentration is the difference of the total arsenic concentration of the acidified sample and the total arsenic concentration of the resin-treated sample.

$\text{H}_2\text{SO}_4$  is used to acidify the sample because  $\text{HCl}$  may create undesirable chloride interference when using the ICP-MS and because there is concern that nitric acid may damage the resin or form nitric acid-arsenic redox couples (Edwards et al., 1997).

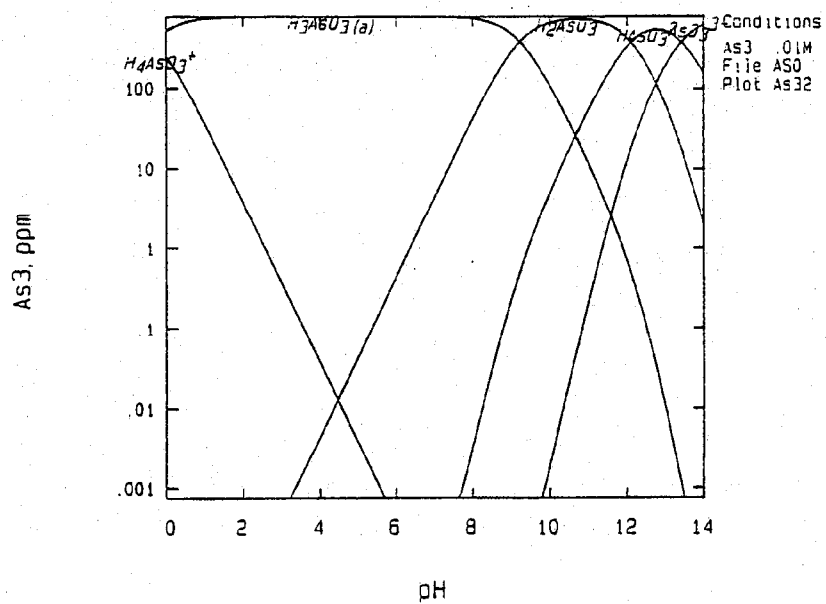


Figure A-1. Solubility Diagram of As (III)

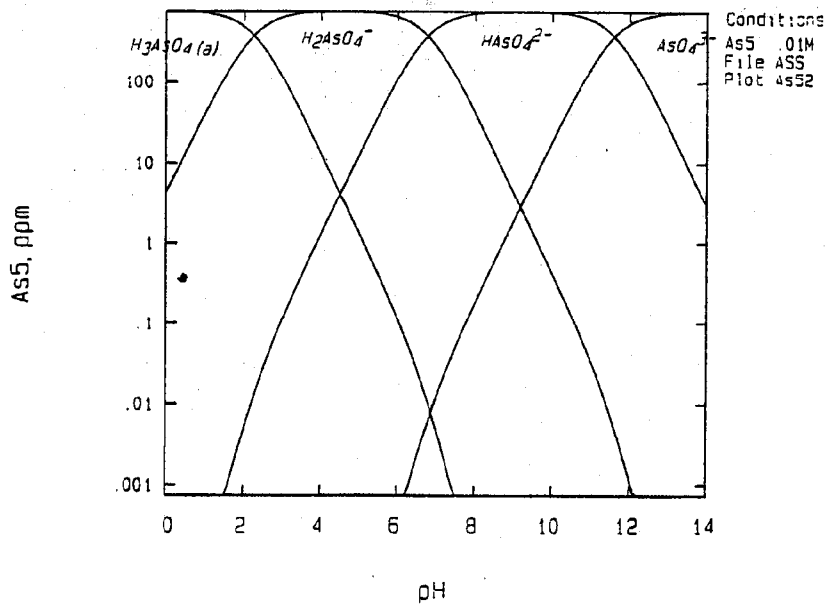


Figure A-2. Solubility Diagram of As (V)

### 3.0 Reagents

Reagents required for field speciation of arsenic include Dowex 1-X8, 50-100 mesh resin, acetic acid, sodium hydroxide (NaOH), and ultra-pure sulfuric acid and nitric acid. All chemicals are of reagent grade or higher.

**3.1 Resin.** Dowex 1-X8, 50-100 mesh resin will be used in this study.

**3.2 Sodium Hydroxide.** One (1) *N* NaOH will be used to prepare the resin.

**3.3 Acetic Acid.** One (1) *N* acetic acid will be used to prepare the resin.

**3.4 Sulfuric Acid.** An ultra-pure sulfuric acid (93-98%, sub-boiling distilled in quartz) will be used to acidify samples prior to the resin treatment.

**3.5 Nitric Acid.** An ultra-pure nitric acid (65%, sub-boiling distilled in quartz) will be used to preserve samples (see Table A-1)

### 4.0 Equipment/Apparatus

**4.1 Resin Preparation.** Dowex 1-X8, 50-100 mesh resin will be converted from the chloride form (as supplied by the manufacturer) to the acetate form before packing into columns. The resin will be prepared in batch according to the method used by Edwards et al. (1997). In summary, one kg of the resin will be placed in a 3-L beaker. One liter of 1 *N* NaOH will be added to the resin, stirred for an hour using an overhead stirrer, and drained. This NaOH rinse will be repeated three times in sequence. The NaOH-treated resin will then be rinsed twice with 1 L of deionized (DI) water, followed by an acetic acid rinse. The acetic acid rinse consists of adding 1 L of 1 *N* acetic acid to the resin, stirring for 5 minutes, and draining. The acetic acid rinse will be repeated three times in sequence. Finally, the mixture will be rinsed with 1 L of DI water three times in sequence.

**4.2 Anion Exchange Column Preparation.** Anion exchange columns will be prepared as described by Edwards et al. (1997). The columns selected for this field speciation method are 12 cm x 15 mm in size and made of polypropylene (Bio-Rad Laboratories, CA). Each column will



be slurry packed with approximately 20 grams (drained weight) of the prepared resin, yielding a resin depth of approximately 10.5 cm. The column will be capped with a plastic cap to prevent contamination prior to use.

**4.3 Beaker.** Four hundred-mL (400-mL) disposable plastic beakers will be used to collect raw water samples. All disposable beakers will be rinsed with DI water and air-dried before being packed into the sampling kits.

**4.4 Syringe and Filter.** Sixty-mL (60-mL) disposable plastic syringes with 0.45- $\mu$ m screw-on filters will be used to filter samples. All disposable syringes and filters will be rinsed with DI water and air-dried before being packed into the sampling kits.

**4.5 Sample Bottles.** VWRbrand™ TraceClean™ HDPE sample bottles (125 mL) labeled A, B and C will be used to contain unfiltered and acidified samples; filtered and acidified samples; and filtered, acidified, and resin-treated samples, respectively. Bottles A and C will contain appropriate amounts of concentrated ultra-pure nitric acid; whereas bottle B will contain 1.25 mL of 5% (volume/volume) ultra-pure sulfuric acid.

## **5.0 Sample Preservation, Containers, Handling, and Storage**

Sample preservation, containers, handling, and storage requirements are indicated in Table A-1. Arsenic speciation at each sampling point in the water treatment process (e.g., inlet, pre-filtration, and outlet) will require collection of three 125-mL bottles identified as bottles A, B, and C, which are defined as follows:

- Bottle A will contain 125 mL of an unfiltered and acidified sample
- Bottle B will contain 125 mL of a filtered sample acidified with 1.25 mL of 5%  $\text{H}_2\text{SO}_4$
- Bottle C will contain 20 mL of a sample obtained by passing some bottle B sample through an anion exchange resin column

**Table A-1. Sample Preservation, Containers, Handling, and Storage**

Sample Bottle Identifier	Sample Size	Container Type	Preservation	Analyte	Holding Time
A	125 mL	Certified HDPE	4°C HNO <sub>3</sub> for pH<2	Total Arsenic by ICP-MS	6 months
B	125 mL	Certified HDPE	4°C 1.25 mL of 5% H <sub>2</sub> SO <sub>4</sub>	Total Arsenic by ICP-MS	6 months
C	20 mL	Certified HDPE	4°C HNO <sub>3</sub> for pH<2	Total Arsenic by ICP-MS	6 months

## 6.0 Procedure

The procedure for processing each arsenic speciation sample includes the following steps:

**6.1 Raw Water Sample Collection.** Completely fill bottle A with the water to be sampled. Cap bottle A and seal the lid with tape.

**6.2 Filtered Sample Collection.** Fill a 400-mL disposable plastic beaker with the water sampled in Section 6.1. Completely fill the syringe with the water from the plastic beaker. Screw the filter snug onto the end of the syringe and push the sample through the filter. Discard the first 10 drops to rinse the filter. Collect the filtered sample in bottle B. Remove the filter, refill the syringe with raw water, reattach the filter to the syringe, and push the sample through the filter into the bottle B. Repeat this process until bottle B is almost full; however, leave a small air gap at the top. The air gap should be approximately 1 to 5 mL. Cap bottle B tightly and shake the bottle for about 15 seconds to ensure thorough mixing. The air gap in the bottle allows the contents to mix thoroughly.

**6.3 Resin-Treated Sample Collection.** Remove the protective cap from the top of the resin column and break off the end at bottom of the resin column. Carefully fill the resin column to the top with the water in bottle B and let the column drain completely. Repeat this process until approximately 40 mL of water from bottle B has been passed through the column. Thereafter, position the resin column over bottle C, fill the column to the top, and let the entire column drain

into bottle C. Repeat this process until approximately 20 mL of resin-treated sample has been collected in bottle C. Cap bottles B and C and seal the lids with tape.

**6.4 Sample Shipping.** After the field speciation is complete, fill out a chain-of-custody form. Place all the sample bottles in a shipper with cold packs and have it shipped to Battelle via FedEx overnight delivery.

**6.5 Arsenic Analysis.** After the samples are received, Battelle will process the samples and perform arsenic analysis using ICP-MS according to EPA 200.8 method. The sample in bottle A will be digested prior to ICP-MS analysis, whereas the samples in bottles B and C will not be digested.

**6.6 Graphic Speciation Procedure.** Figure A-3 provides a graphic description of the field speciation procedure which is designed to assist plant POCs to follow the procedure more easily.

## 7.0 Calculations

For each As speciation sampling event, three sample bottles (A, B, and C) will be produced and the water in these bottles will be analyzed for total arsenic by ICP-MS. Total arsenic (including particulate arsenic), total particulate arsenic, total soluble arsenic, As (III), and As (V) will be calculated as follows:

- **Total Arsenic (including particulate arsenic)** = total arsenic concentration in bottle A
- **Total Soluble Arsenic** = total arsenic concentration in bottle B
- **Total Particulate Arsenic** = total arsenic concentration in bottle A – total arsenic concentration in bottle B
- **As (III)** = total arsenic concentration in bottle C
- **As (V)** = total arsenic concentration in bottle B – total arsenic concentration in bottle C

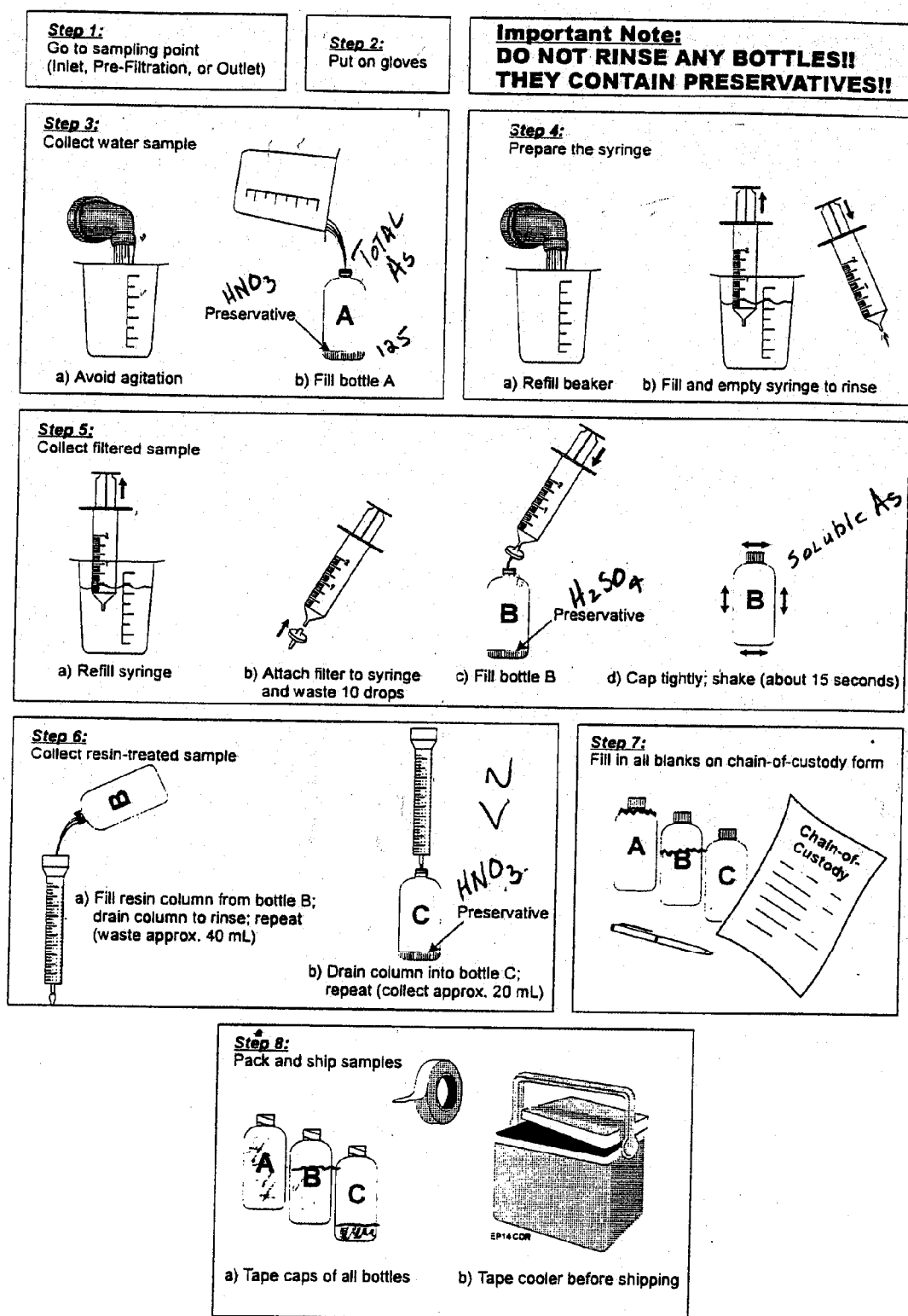


Figure A-3. Arsenic Field Speciation Procedure

## 8.0 ICP-MS Quality Control

As required by EPA Method 200.8, Battelle's ICP-MS laboratory performed a quality control (QC) check, including an initial demonstration of laboratory capacity and periodic analyses of laboratory reagent blanks, fortified blanks, and calibration solutions as a continuing check on performance. A 5-point calibration was performed using certified As standard solutions with concentrations of 0.1, 5, 10, 30, and 50 µg/L. A linear calibration range of 0.1 to 50 µg/L was established with a correlation coefficient greater than 0.999. A method detection limit (MDL) was established to be 0.02 µg/L.

DI water and two source water samples including a groundwater and a surface water collected from two local water treatment plants were spiked with 10 µg/L of the As standard. A series of samples including QC samples (a calibration blank, calibration standards, quality control standards, and a laboratory fortified blank) were analyzed in a sequence shown in Table A-2. All percentage recoveries and relative percent difference (%RPD) values presented in Table A-2 are within the QC limits required by the Method 200.8.

**Table A-2. ICP-MS Quality Control Check**

Sample Sequence	Concentration	Percent Recovery	% RPD
Calibration Blank	+0.055		
Calibration Standard 2	4.94	99%	
Calibration Standard 4	29.0	97%	
Quality Control Standard	26.8		
Quality Control Standard	26.4		
Quality Control Standard	26.9		
Average	26.7	107%	0.9%
Laboratory Fortified Blank	8.07	101%	
DI Water (Laboratory Reagent Blank)	0.032		
DI Water Spiked with 10 µg/L As	9.56		
Ground Water	0.725		
Ground Water Spiked with 10 µg/L As	10.7		
Surface Water	1.19		
Surface Water Spiked with 10 µg/L As	9.80		
Quality Control Standard	63.7	106%	
Calibration Blank	-0.018		
Calibration Standard 2	5.22	104%	
Calibration Standard 4	28.9	96%	
Quality Control Standard	26.3	105%	
Laboratory Fortified Blank	7.92	99%	

## 9.0 Verification of Arsenic Speciation Method

Verification of the arsenic speciation method was performed in Battelle's laboratories using sodium arsenite ( $\text{NaAsO}_2$ ) and disodium hydrogen arsenate heptahydrate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ) as As (III) and As (V) model compounds. The source water used in the ICP-MS QC check was also used in the verification study to more closely mimic field conditions.

DI water was spiked with 10 or 50  $\mu\text{g/L}$  of an As (III) or an As (V) standard solution.

Groundwater and surface water were spiked with 10 or 50  $\mu\text{g/L}$  of the As (V) standard. The pH of each solution was adjusted to 2, 3, or 4 using an ultra-pure sulfuric acid. Thereafter, the procedure described in Section 6.0 was followed. The samples before and after the resin column treatment were analyzed for total arsenic by ICP-MS.

The results show that the recoveries of As (III) from the resin columns ranged from 93.2 to 97.3%. The amount of As (V) retained in the resin columns ranged from 91.5 to 100%. The results also indicate that the difference in arsenic recovery/retention between the samples of pH 2 and the samples of pH 4 was less than 6%.

## 10.0 References

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